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(54) Title: RESIN AND ROSIN EMULSIONS

(57) Abstract

A self-emulsifying resin or rosin composition and a process for the production thereof, which composition comprises as a main component rosin, or a derivative thereof, or a hydrocarbon resin based on C_5 to C_9 hydrocarbons, or a mixture of these, and that it further comprises a reaction product of an ethoxylated phosphorus containing surface active compound and a base. The phosphorus containing surface active compound is an organic phosphate ester and the base is a nitrogen containing base. The composition is used as a tackifier composition for adhesives.

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RESIN AND ROSIN EMULSIONS

This invention relates to self-emulsifying resin or rosin compositions and their preparation. The resin or rosin composition can be used as a tackifier resin, for example in conjunction with a polymer latex, as adhesives.

It is common to include tackifiers when formulating an adhesive composition among other things to increase the tack of the binder. The tack of an adhesive enables it to form an immediate bond between contacted surfaces when they are brought together.

Tackifier resins can be divided mainly into two groups, rosin and derivatives thereof and hydrocarbon resins. In aqueous based adhesives, usually the rosin and resin are prepared in the form of a solvent based solution or in the form of an aqueous emulsion and then combined with a polymer latex.

Rosin and resin emulsions have previously been made by first melting the resin or rosin, then adding an emulsifying system and water to form an emulsion, in which the rosin/resin is the dispersed phase and water, the continuous phase. Storage of the rosin/resin component at elevated temperature, for example 130° can result in degradation, and if an aqueous solution of an emulsifier is incorporated as well into the rosin/resin the further degradation will occur, if the rosin has been allowed to cool, and then reheated, due to the loss by evaporation of water.

After storage and any necessary reheating, the composition is combined with water to form a water-in-oil emulsion. Addition of more water is necessary to bring about inversion of this emulsion, to form an oil-in-water emulsion which, if desired, can be subsequently combined with a polymer latex to form an adhesive in which the rosin or resin component acts as a tackifier. Examples of the emulsifiers used in these compositions are surfactant materials, such as e.g. ethoxylated sulphur derivatives or salts thereof.

The method of preparation of these emulsions is

lengthy with first making the water in oil emulsion and then the final oil in water emulsion. It is also a disadvantage from an economical point of view to send an emulsion, containing a lot of water, from the producer to the user of the rosin or resin tackifier.

It is accordingly an object of the present invention to obtain a resin or rosin composition which is stable at storage at an increased temperature.

It is further an object of the invention to obtain a resin or rosin composition with a much simpler method of preparation.

It is further an object of the present invention to obtain a resin or rosin composition which is more easy to handle during transportation.

The objects of the invention are achieved by a process, as claimed in the claims, in which a self-emulsifying resin or rosin composition is prepared. The self-emulsifying composition comprises as a main component rosin, or a derivative thereof, or a hydrocarbon resin based on C_5 to C_9 hydrocarbons, or a mixture of these. It further comprises a reaction product of an ethoxylated phosphorus containing surface active compound and a base.

It was surprisingly found that a stable and self-emulsifying resin or rosin composition can be produced if the mentioned emulsifier and a base are formed into a premix, in which they are allowed to react and which is subsequently dispersed into the molten resin or rosin. The resulting composition is self-emulsifying in that it can be combined with a polymer latex to form an adhesive composition.

The present invention accordingly provides a method of forming a composition containing a resin or rosin, an emulsifier and a base, the method comprising first combining the emulsifier and the base, allowing them to interact, then dispersing the resulting mixture into the premelted resin or rosin.

The invention also provides a composition made by this method.

The product composition formed is a stable solid which can be stored at or above room temperature for prolonged periods and which, after re-melting if necessary, disperses upon simple admixture with a polymer latex, to form an adhesive.

The rosin used in the invention can, in general, include any form of rosin or rosin derivative.

Another class of resins which can be used in this invention is that consisting of hydrocarbon resins based on C_5 to C_9 hydrocarbons.

Rosin is a solid resinous material which occurs naturally in the oleoresin of pine trees. It is obtained from one of three main sources, namely the oleoresin exudate of living pine trees, the oleoresin contained in the aged stumps of pine trees and the tall oil produced as a by-product in the kraft paper industry. In addition to cyclic terpene carboxylic acids, rosins also includes a small amount of non-acidic components.

A major constituent of rosin is abietic acid, which is a tricyclic doubly-unsaturated mono-carboxylic acid. Abietic acid undergoes Diels-Alder addition reactions with dienophiles. Rosin may therefore be reacted with dienophilic carboxylic acids and their derivatives, such as maleic acid, acrylic acid, maleic anhydride and fumaric acid, and so forms tertracyclic polycarboxylic acids. This reaction between rosin and dienophiles is commonly termed "fortification" and the reaction product is commonly termed a "fortified" rosin. Fortified rosin dispersions are used as sizing compositions in the paper sizing industry. Compositions according to the present invention may be based upon rosin, a fortified rosin or a mixture of the two. It is also possible to employ fortified rosins which have been treated with formaldehyde in order to enhance their stability. Esterified or disproportionated rosins may also be used in the compositions of this invention. Esterified rosins are rosins which have been reacted with an alcohol, preferably a polyol such as glycerol, triethylene glycol or pentaerythritol. Disproportionated rosins are rosins

which have been treated by a catalytic process in order to improve their stability to oxidation. Hydrogenated rosins may also be used, again to give improved stability to oxidation, as may ester derivatives of fortified, disproportionated and hydrogenated rosins.

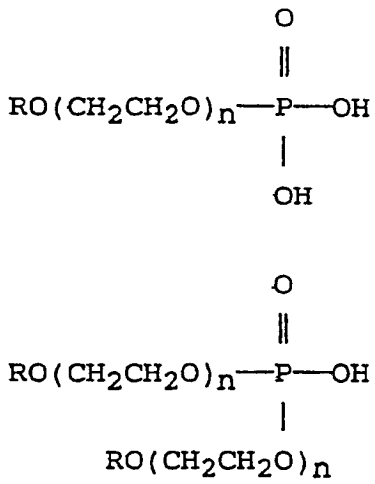
The preferred rosins for use in the composition of this invention are stabilized rosins, stabilized rosin derivatives, however non stabilized forms can be used. Another preferred feature of the invention lies in the use of acrylic-modified rosins. Rosins and rosin derivatives which have been reacted with phenolic resins. e.g. phenol-formaldehyde resins, are also suitable. The softening point range of any of the types of rosin, rosin derivative, hydrocarbon resin used would be from 0°C to 160°C.

Mixtures of any of the resins, rosins and rosin derivatives mentioned above may be used in the compositions of this invention.

Another optional feature is the use of rosin dispersions in the form of a soap, which may be formed in situ by the neutralization of part of the total acidity of the rosin, using either an organic or inorganic base. Preferably, such procedures involve the neutralization of amount in the range from 1% to 10% and, more preferably, from 3% to 6% of the total acidity of the rosin acids. This procedure does not result in the formation of a water-soluble rosin or rosin derivative but rather in the convention of a proportion of the resin or rosin derivative into the soap which then acts to form an aqueous dispersion of the rosin or rosin derivative which would otherwise neither dissolve nor disperse in water.

In this specification the term "rosin" is to be construed to include all the types of rosins and rosin derivatives, including those mentioned above, and all mixtures thereof.

The phosphorous containing surface active compound used to produce the self-emulsifying composition is an organic phosphate ester having the general formulae:



or

and mixtures thereof

wherein R represents an alkyl, an alkyl phenol, alkenyl or alkaryl group comprising from 5 to 20 carbon atoms and n has a value of from 5 to 20. It is preferred to use a phosphate ester in which R is nonyl phenyl and n having a value of from 7 to 14, most preferably with n having a value of 9.5. The phosphate esters are liquids and are used as such and not in the form of a water solution which is often normal with other surface active compounds.

The base used for forming a reaction product with the phosphate esters is a nitrogen containing base such as alkanol amines e.g. mono, di or tri ethanolamine, diamino ethanol, morpholine or ammonia.

It is important to combine the phosphate ester and the base prior to addition of these components to the resin/rosin. If the phosphate ester and the base are added separately to the rosin a stable self-emulsifying resin/rosin with the above mentioned advantages will not be obtained. The base is added to the liquid phosphate ester and the components are allowed to interact and then the resulted liquid mixture is added to the resin/rosin. The resulted liquid mixture being a hundred per cent liquid and not in the form of a water solution. Thus, when added to the hot melted rosin there is no water being evaporated. The resultant resin/rosin, emulsifier mixture can be stored at or above room temperature for prolonged periods. The

mixture can be used as such in a polymer latex. It is not necessary to first form an oil in water dispersion, but it is possible to directly disperse the polymer latex in the resin/rosin composition.

Advantageously, composition according to the invention also contain a protective colloid, for example casein, in addition to the emulsifier already mentioned.

The resin or rosin content of the resin/rosin-emulsifier-base compositions of the present invention is preferably from 75 to 98% by weight, more preferably 87 to 95% by weight, of the composition.

The concentration of the reaction product of phosphate ester and base is in the range of 2 to 20 parts by weight per 100 g of resin/rosin, preferably within the range of 4 to 15 parts by weight per 100 g of resin/rosin.

Of the total composition the phosphate ester content is preferably from 1 to 15% by weight, more preferably 3 to 8% by weight, and the base is preferably present in an amount of from 1 to 10% by weight, more preferably 2 to 5% by weight, of the composition.

Compositions according to the invention can also have improved thermal stability, up to 150° for example, compared with the known resin/rosin-emulsifier compositions, as mentioned above. The compositions can accordingly be readily transportable, since they will normally be solids. The dispersion formed with the latex can have a relatively high solids content and so also can be transported readily.

Although nor necessary because of their self-emulsifying properties, compositions according to the invention can, if desired, be formed into adhesives by first combining them with water to form an oil-in-water emulsion and then combining this with a polymer latex to form the adhesive. Formation of the adhesive is thus simplified even when this procedure is followed.

The self-emulsifying resin or rosin composition according to the invention can be used as a tackifier composition in combination with a polymer latex as adhesives, for example as pressure sensitive adhesives and

flooring adhesives. The polymer latex used can be based on a lot of different polymers such as acrylic polymers, styrene-butadiene rubbers, ethylene-vinyl acetate and polyvinyl acetate and polychloroprene. The amount of tackifier used when formulating the adhesive composition is different for different polymers and different use. The following values can be mentioned: The adhesive composition comprises 40 - 90 parts by weight of a polymer latex and 60 - 10 per cent by weight of the self-emulsifying resin or rosin composition.

The invention will now be described further by way of the following examples, in which all parts are by weight.

EXAMPLE 1 (COMPARISON)

100 parts of disproportionate rosin was melted by heating to 100°C. To the molten rosin, 8 parts of a nonylphenylethoxylated phosphate ester surfactant was added, followed by 2.5 parts of triethanolamine. Addition of 100 parts of water batchwise resulted in initial formation of water-in-oil emulsion and subsequent inversion into an oil-in-water emulsion. 100 parts of the inverted emulsion was combined with 100 parts of a styrene butadiene rubber latex to give a pressure-sensitive adhesive.

EXAMPLE 2

The same amounts of the same rosin, surfactant and base as in Example 1 were used but the surfactant and triethanolamine were first mixed together before being added to the molten rosin.

EXAMPLE 3

The procedure of Example 2 was followed with a stabilized rosin ester replacing the disproportionate rosin.

EXAMPLE 4

100 parts of water were added to 110.5 parts of the compositions of Example 2 and 3 to produce oil-in-water

emulsions directly.

EXAMPLE 5

100 parts of a styrene butadiene rubber latex were added to 100.5 parts of the compositions of Example 2 and 3 to produce pressure-sensitive adhesives directly.

EXAMPLE 6

The procedure of Example 5 was followed with an acrylic latex replacing the styrene butadiene rubber latex.

EXAMPLE 7

The thermal stabilities of the rosin-emulsifier-base composition of Example 1 and that of Example 2 were tested by heating the respective compositions to the following temperatures. The compositions were found to be thermally stable over the time periods shown below.

Temperature (°C)	Example 1	Example 2
130	unstable	> 5 hours
140	< 1 hour	> 5 hours
150	unstable	2 hours

EXAMPLE 8

The following were mixed and allowed to react

water	17.5 parts
triethanolamine rosin soap (75%)	4 parts
surfactant	3 parts
triethanolamine	4 parts
casein	1.5 parts

before being heated to 30°C and added to 100 parts of Burez 301 rosin which had been preheated to 100°C. The resulting emulsion was blended with sufficient water to give a solids content of 50%.

EXAMPLE 9

The following were mixed and allowed to react

surfactant	3	parts
triethanolamine	3	parts

before being heated to 30°C and added to 100 parts of Burez 301 rosin which had been preheated to 100°C. The resulting emulsion was combined with the following mixture

water	19.5	parts
triethanolamine rosin soap (75%)	4	parts
casein	1.5	parts

and further water added to give a solids content of 50%.

EXAMPLE 10

An initial rosin-surfactant-base mixture was formed as in Example 9. This emulsion was then combined with the following mixture

water	14.5	parts
triethanolamine	1.0	parts
casein	1.5	parts

and further water added to give a solids content of 50%.

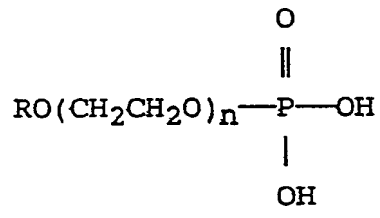
The final emulsions of Example 8, 9 and 10 were each blended with a styrene butadiene or acrylic rubber latex to provide an adhesive.

The surfactant used in each of Example 8, 9 and 10 was a nonylphenylethoxylated phosphate ester, as in Example 1 to 6.

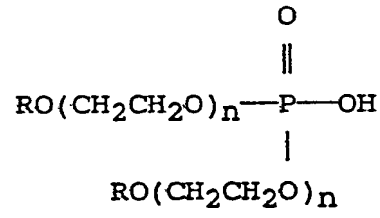
Claims

1. A self-emulsifying resin or rosin composition, characterized in that it comprises as a main component rosin, or a derivative thereof, or a hydrocarbon resin based on C_5 to C_9 hydrocarbons, or a mixture of these, and that it further comprises a reaction product of an ethoxylated phosphorus containing surface active compound and a base.

2. A composition according to claim 1, characterized in that the phosphorous containing surface active compound is an organic phosphate ester having the general formulae:



or



and mixtures thereof
wherein R represents an alkyl, an alkyl phenol, alkenyl or alkaryl group comprising from 5 to 20 carbon atoms and n has a value of from 5 to 20.

3. A composition according to claim 1, characterized in that the base is a nitrogen containing base such as alkanol amines e.g. mono, di or tri ethanolamine, diamino ethanol, morpholine or ammonia.

4. A composition according to claim 1, characterized in that the main component is rosin and/or a derivative thereof.

5. A composition according to any of the preceding claims, characterized in that it comprises from 80 to 98 per cent by weight of the main component and from 2 to 20

per cent by weight of the reaction product, based on the composition.

6. A composition according to any of the preceding claims, characterized in that it further comprises a protective colloid.

7. A process for the preparation of a self-emulsifying resin or rosin composition, characterized in that an ethoxylated phosphorus containing surface active compound and a base are first reacted and the obtained reaction product is then dispersed into the pre-melted main component which is rosin, or a derivative thereof, or a hydrocarbon resin based on C_5 to C_9 hydrocarbons, or a mixture of these.

8. Use of a self-emulsifying resin or rosin composition, which comprises as a main component rosin, or a derivative thereof, or a hydrocarbon resin based on C_5 to C_9 hydrocarbons, or a mixture of these, and which further comprises a reaction product between an ethoxylated phosphorus containing surface active compound and a base, as a tackifier composition for adhesives.

9. Use according to claim 7, whereby the composition is combined with a polymer latex.

10. Use according to claim 9, whereby the composition is first emulsified in water before incorporation in the latex to form an adhesive.

11. Adhesive composition, characterized in that it comprises 40 to 90 parts by weight of a polymer latex and 60 to 10 parts by weight of a self-emulsifying resin or rosin composition, which comprises as a main component rosin, or a derivative thereof, or a hydrocarbon resin based on C_5 to C_9 hydrocarbons, or a mixture of these, and which further comprises a reaction product of an ethoxylated phosphorus containing surface active compound and a base.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00483

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 L 93/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 L; B 01 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP, A2, 0084829 (HERCULES INCORPORATED) 3 August 1983, see the whole document --	1,11
A	Chemical Abstracts, volume 101, no. 12, 17 September 1984, (Columbus, Ohio, US), see page 55, abstract 92239q, & JP, A, 5980467 (Rosin ester emulsions) 9 May 1984 --	1,11
A	Chemical Abstracts, volume 108, no. 12, 21 March 1988, (Columbus, Ohio, US), see page 126, abstract 96669x, & HU, A, 40930 (Emulsifier composition based on pine resin and its derivatives) 30 March 1987 --	1

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* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17th October 1991	1991 -10- 21
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Dagmar Järvman

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 91/00483

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 91-08-30
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0084829	83-08-03	CA-A-	1176389	84-10-16
		JP-B-	2054387	90-11-21
		JP-A-	58127758	83-07-29